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ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: **REFORMING CATALYST**

(57) Abstract: A reforming catalyst comprising precious metal particles dispersed on a support material, wherein the precious metal particles comprise rhodium or ruthenium, wherein the support material comprises ceria and zirconia dispersed on the surface of a silica-alumina material, and wherein the loading of the ceria and zirconia is 10-60wt % based on the weight of the support material is disclosed. The catalyst shows excellent sulphur tolerance. Catalysed components and fuel processing systems comprising the catalysts, and reforming processes using the catalysts are also disclosed.



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REFORMING CATALYST

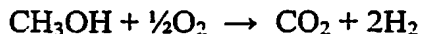
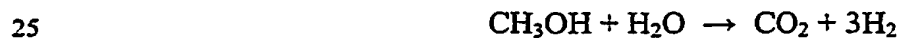
The present invention relates to fuel reforming catalysts, catalysed components
5 and fuel processing systems comprising the catalysts, and reforming processes using the catalysts.

Hydrogen is an important industrial gas and is used in a number of applications
such as ammonia synthesis, methanol synthesis, chemical hydrogenations, metal
10 manufacture, glass processing and fuel cells. Fuel processors produce hydrogen by reforming fuels such as methane, propane, methanol, ethanol, natural gas, liquefied petroleum gas (LPG), diesel and gasoline, and are used to provide hydrogen for a variety of applications, particularly for fuel cells. The reforming process produces a hydrogen-rich reformat stream that also comprises carbon dioxide, carbon monoxide and trace
15 amounts of hydrocarbons or alcohols. Carbon monoxide is a severe poison for the catalysts in the anode of a fuel cell, so fuel processing systems generally comprise a fuel reformer and one or more carbon monoxide clean-up stages.

In a steam reforming process, water and fuel are combined to produce hydrogen
20 and carbon dioxide, e.g. for methanol:



This process is endothermic, so steam reforming requires a continuous input of energy. In an autothermal reforming process, both water and air are mixed with the fuel. The process combines steam reforming and partial oxidation, e.g. for methanol:



The partial oxidation is exothermic, thus providing the heat for the endothermic steam reforming reaction. Another reaction which may take place within the autothermal reformer is the water gas shift reaction:



This is a particularly useful reaction because it reduces CO content and increases hydrogen content. Autothermal reforming processes are described in WO 96/00186.

Catalysts are used to promote the various reforming reactions. Generally the
35 catalysts comprise metal particles deposited on ceramic support materials. A commonly

used support material is γ -Al₂O₃ due to its mechanical stability, moderately high surface area, resistance to sintering over a wide range of temperatures and high degree of metal dispersion that can be achieved. EP 1 157 968 discloses a catalyst for use in autothermal reforming reactions which contains rhodium and optionally platinum on an active aluminium oxide. JP 2002 336702 discloses an autothermal reforming catalyst comprising rhodium and caesium on a support consisting of 10wt% ceria dispersed on silica-alumina.

Desirably the catalysts promote the reforming reactions over a wide temperature range and for a variety of fuels. The catalyst should be durable, i.e. the performance should not decrease significantly with time. One factor that can decrease catalyst performance and durability is the presence of sulphur within fuels. Fuels such as gasoline, diesel and natural gas contain levels of sulphur up to 150ppm and this is a poison for many state-of-the-art reforming catalysts. Another factor that can decrease catalyst performance is deposition of carbon particles onto the catalyst.

To avoid sulphur poisoning, the sulphur can be removed from a fuel before it is added to a fuel processing system, but this will significantly increase the cost of the fuel. Alternatively a fuel processing system can comprise a desulphurisation unit, which contains a sulphur trap material. The unit may be located before or after the reformer, or before or between the CO clean-up units. However, the inclusion of a desulphurisation unit increases the complexity, size and cost of the fuel processing system. Another approach is to periodically replace or regenerate catalysts that have been poisoned by sulphur. This can interrupt hydrogen generation and the replacement of catalysts may be costly. A preferred approach is to develop catalysts that are intrinsically sulphur tolerant and are not poisoned by the amounts of sulphur commonly found in fuels such as gasoline. It is an object of the present invention to provide a reforming catalyst with improved sulphur tolerance. The catalyst should also demonstrate high performance and durability. It is a further object of the present invention to provide a reforming catalyst wherein carbon deposition is decreased.

Accordingly the present invention provides a reforming catalyst comprising precious metal particles dispersed on a support material, wherein the precious metal

particles comprise rhodium or ruthenium, wherein the support material comprises ceria and zirconia dispersed on the surface of a silica-alumina material, and wherein the loading of the ceria and zirconia is 10-60wt% based on the weight of the support material.

5

The present inventors have found that the catalysts according to the invention show excellent sulphur tolerance and minimal carbon deposition.

The weight ratio of silica:alumina in the support material is suitably between 10 1:100 and 100:1, preferably between 5:100 and 1:1. The silica-alumina material may contain regions of silica, regions of alumina and/or regions of mixed silicon/aluminium oxide. The silica-alumina material may contain other components, but preferably contains only silica, alumina and mixed silicon/aluminium oxide. In a preferred embodiment, the surface of the silica-alumina material is silica rich and the centre of the 15 silica-alumina material is alumina rich. Suitable silica-alumina materials and their manufacture are described in US 5,045,519 and are available from Sasol GmbH (Brunsbuttel, Germany). The surface area of the silica-alumina material is suitably above 100 m²/g, preferably above 150m²/g, most preferably above 200m²/g.

20 The loading of ceria and zirconia (i.e. the combined mass of the ceria and the zirconia as a percentage of the total mass of the support material) is 10-60wt%, preferably 25-60wt%. The ceria and zirconia may be present as regions of ceria, regions of zirconia and/or regions of mixed ceria-zirconia oxide. It is preferred that the majority of the ceria and zirconia is present as the mixed oxide. The atomic ratio of ceria:zirconia 25 is suitably in the range from 10:1 to 1:10, preferably from 5:1 to 1:1, most preferably about 3:1. The average particle size of the ceria and zirconia particles on the surface of the silica-alumina material is suitably below 15nm, preferably below 8nm.

The precious metal particles comprise rhodium or ruthenium. The precious metal 30 particles may be rhodium or ruthenium alone, or may be alloy particles comprising rhodium and/or ruthenium. Suitable alloying metals include other precious metals such as platinum, palladium, osmium or iridium, preferably platinum, but may also include base metals. In a preferred embodiment the precious metal particles are rhodium

particles or platinum-rhodium alloy particles. In a particularly preferred embodiment the precious metal particles are rhodium particles.

The precious metal particles are dispersed on the support material. The precious metal particles may be deposited on the silica-alumina material, on the ceria-zirconia particles and/or at the interfaces of the ceria-zirconia and the silica-alumina. Suitably the loading of the precious metal particles is 0.5-10 weight %, based on the weight of the support material. If the precious metal particles are platinum-rhodium alloy particles, a suitable atomic ratio of platinum:rhodium is between 5:1 and 1:5, preferably about 1:1.

In a preferred embodiment, the reforming catalyst further comprises an alkali metal or alkaline earth metal promoter, preferably lithium. The promoter is deposited on the surface of the support material and is preferably alloyed with the precious metal particles. The atomic ratio of precious metal particles to promoter material is suitably between 20:1 and 5:1.

The catalyst may be prepared by any suitable methods known to those skilled in the art. Suitable methods include co-impregnation, deposition precipitation and co-precipitation procedures.

A suitable method for preparing the support material is the deposition of ceria and zirconia onto a silica-alumina material by a sol-gel route. The method uses sols of ceria and zirconia, which are stabilised by counter ions such as nitrate and acetate. Suitable sols are available from Nyacol Nano Technologies Inc. (Ashland, MA, USA). The counter ion to metal ratio is suitably in the range from 0.1:1 to 2:1. The metal oxide content is suitably between 100 and 500g/l and the average particle size is suitably from 1-100nm. The sols are added to a slurry of a silica-alumina support material. A base such as 1M ammonia solution is added to the slurry. The product is then washed several times, dried, eg at 120°C and calcined, eg at 800°C.

A suitable method for the deposition of the precious metal particles onto the support material is co-impregnation. Suitable metal salts are made up into a solution such that the volume of solution is sufficient to fill the entire pore volume of the support

material. The solution is added to the support material, the material is mixed thoroughly and then dried and calcined. An alternative, but lengthier, method is to sequentially impregnate the different metal species.

5 Another suitable method for the deposition of the precious metal particles is co-deposition. The support material is dispersed in a slurry containing suitable precious metal salts. A base is added to deposit the metal onto the support material, and the catalyst is dried and calcined.

10 In a further aspect, the present invention provides a catalysed component comprising the reforming catalyst according to the invention. The catalysed component comprises the reforming catalyst deposited on a suitable substrate. The substrate may be any suitable flow-through substrate such as a monolith, foam, static mixer or heat exchanger unit. Alternatively the substrate may comprise discrete units such as pellets,
15 rings etc. which are enclosed in a container. The substrate may be ceramic, eg cordierite, or metallic. The amount of catalyst on the substrate is suitably from 0.5-5g/in³ (0.03-0.3g/cm³).

 The catalyst is deposited on the substrate using any appropriate techniques known
20 to those skilled in the art. Suitably, the catalyst is dispersed in water, possibly with additional binders, thickeners or adhesive agents to form a slurry. It is usually necessary to break down the particle size of the catalyst by milling the slurry, e.g. in a ball mill or a bead mill, or by milling the dry catalyst before it is added to the slurry, e.g. in a jet mill. The slurry is passed over or through the substrate to coat the surfaces that will be
25 exposed to the reactant gases. This can be done by dip coating, flood coating or waterfall coating. These and other methods, such as vacuum impregnation, are well known in the art. Any excess slurry is removed, and the substrate is subsequently dried and calcined.

30 In a yet further aspect, the present invention provides a process for reforming fuel using a catalysed component according to the invention. The process comprises the step of supplying fuel, steam and optionally air to the catalysed component. The fuel may comprise up to 150ppm sulphur. The fuel may be an alkane such as methane, an alcohol

such as methanol or a mixture of components, such as gasoline. Liquid fuels must be vaporised before they are supplied to the catalysed component. If the process uses steam reforming (and not autothermal reforming), heat must be supplied to the reaction or to the catalysed component, e.g. by pre-heating the fuel and/or steam.

5

In a yet further aspect, the present invention provides a fuel processing system comprising a catalysed component according to the invention. The system may further comprise carbon monoxide clean-up components (e.g. water gas shift reactors, selective oxidation reactors, hydrogen diffusion membranes), heat exchanger components and catalytic burners.

10

The invention will now be described by reference to examples which are not meant to be limiting thereof.

15

Catalyst Manufacture

Eleven different catalysts were prepared:

	Support	Catalytic metal
Comparative Catalyst 1	30wt% ceria and zirconia on alumina (SCF-140)	2wt% rhodium Lithium promoter (Rh:Li molar ratio of 10:1)
Catalyst 1	30wt% ceria and zirconia on silica-alumina (Siralox 10/360)	2wt% rhodium Lithium promoter (Rh:Li molar ratio of 10:1)
Catalyst 2	40wt% ceria and zirconia on silica-alumina (Siralox 10/360)	2wt% rhodium Lithium promoter (Rh:Li molar ratio of 10:1)
Comparative Catalyst 2	Silica-alumina (Siralox 10/360)	1wt% rhodium
Catalyst 3	10wt% ceria and zirconia on silica-alumina (Siralox 10/360)	1wt% rhodium
Catalyst 4	30wt% ceria and zirconia on silica-alumina (Siralox 10/360)	1wt% rhodium
Catalyst 5	40wt% ceria and zirconia on silica-alumina (Siralox 10/360)	1wt% rhodium

	Support	Catalytic metal
Catalyst 6	60wt% ceria and zirconia on silica-alumina (Siralox 10/360)	1wt% rhodium
Catalyst 7	30wt% ceria and zirconia on silica-alumina (Siralox 10/360)	2wt% rhodium
Catalyst 8	40wt% ceria and zirconia on silica-alumina (Siralox 10/360)	2wt% rhodium
Catalyst 9	60wt% ceria and zirconia on silica-alumina (Siralox 10/360)	2wt% rhodium

The alumina and the silica-alumina were purchased from Sasol GmbH (Brunsbuttel, Germany). The amount of silica in the Siralox 10/360 is 10wt%. The alumina or silica-alumina materials were slurried in demineralised water, and nitrate-stabilised ceria and zirconia sols were added. Ammonia solution (1M) was added until the pH of the slurry reached 8. The product was filtered and washed several times to remove NH_4NO_3 and then dried at 120°C for 8 hours and calcined at 800°C for 2 hours. The ceria:zirconia ratio in all the catalysts was 3:1.

A co-impregnation method was used to deposit the rhodium and lithium onto the support material. Rhodium nitrate (Johnson Matthey, UK) and lithium nitrate (BDH, AnalaR® grade) were made up into an aqueous solution such that the volume of solution was sufficient to fill the entire pore volume of the support material. The solution was added to the support material, the material was mixed and then the material was dried at 120°C for 8 hours and calcined at 500°C for 2 hours.

Catalysed Component Manufacture

The catalysts were deposited onto cordierite monoliths with cell densities of 900 cells per square inch (equivalent to 140 cells per square centimetre) and 1200cpsi (186 cells per cm^2) using the following general method:

The catalyst was dispersed in water, providing a slurry with a solid content of about 35wt%. A hydroxyethylcellulose thickener (Natrosol, Hercules) was added to the

slurry at a loading of 0.05wt% with respect to the weight of the slurry. The slurry was mixed using a Silverson mixer, and milled using a bead mill.

The slurry was applied to the monoliths using a vacuum impregnation process. The slurry was applied to one of the open surfaces of the monolith, and a vacuum was applied to draw the slurry into the monolith. The monolith was dried and then slurry was applied to the second open surface of the monolith, using the same method. The monolith was dried at 120°C and subsequently calcined at 500°C for 4 hours.

The loading of catalyst on each monolith was 2g/in³ (0.12g/cm³).

Performance Tests

A pre-heated mix of steam, fuel and air was passed over the catalysed components and the product stream was dried using condensers and a Signal drier unit before analysis by a micro-gas chromatograph. The non-methane hydrocarbon (NMHC) level was measured as an indication of how effectively the catalysed component has reformed the fuel. A low level of NMHC indicates high conversion and an effective catalyst. In several experiments, the CO₂:CO ratio was also measured. This represents the ability of catalyst to convert CO to H₂ via the water gas shift reaction, thus providing lower CO levels.

Test 1: Sulphur tolerance

Two catalysed components were tested. Comparative Example 1 was a 900cpsi cordierite monolith coated with comparative catalyst 1 at a loading of 2g/in³. Example 1 was a 900cpsi cordierite monolith coated with catalyst 1 at a loading of 2g/in³. The monoliths were cored to give cylindrical catalysed components of length 3in (7.5cm) and diameter 1.4in (3.5cm).

The pre-heated mix of steam, fuel and air was passed over the catalysed components at a gas hourly space velocity of 75000h⁻¹. The ratio of the gases was O₂:C = 0.4 and H₂O:C = 2 (where C is moles of carbon, not moles of fuel). The pressure was

1bara (1 bar absolute), i.e. atmospheric pressure. The temperature at the gas outlet was ramped from 700°C to 730°C to 760°C during the course of the six hour test. The fuel was a complex mix gasoline comprising 10ppm sulphur.

Figure 1 shows the NMHC levels for comparative example 1 and example 1. It is clear that the catalyst according to the invention performs significantly better across the temperature range than the catalyst based on a ceria/zirconia/alumina support, indicating improved sulphur tolerance.

Test 2: Sulphur tolerance

Three catalysed components, examples 2, 3 and 4, were tested. Examples 2, 3 and 4 were 900cpsi cordierite monoliths coated with catalyst 1 at a loading of 2g/in³. The monoliths were cored to give cylindrical catalysed components of length 3in (7.5cm) and diameter 1.4in (3.5cm).

The tests were run under the same conditions as for Test 1 except that different fuels were used. Example 2 was tested using simple gasoline-like fuel (having similar physical properties to commercial gasoline, eg density, octane number) with 0ppm sulphur. Example 3 was tested using complex mix gasoline with 10ppm sulphur (as used in Test 1). Example 4 was tested using commercial gasoline with 100ppm sulphur.

Figure 2 shows the NMHC levels for examples 2, 3 and 4. The results show that a sulphur level of 10ppm has no affect on the catalyst according to the invention (the performance for example 3 is equivalent to the performance for example 2). A sulphur level of 100ppm does cause a performance decrease at low temperature (700°C), but overall the NMHC level is still low for such a high level of sulphur.

Test 3: Durability

Three catalysed components were tested. Comparative example 2 was a 1200cps i cordierite monolith coated with comparative catalyst 1 at a loading of 2g/in³. Example 5 was a 1200cps i cordierite monolith coated with catalyst 1 at a loading of

2g/in³. Example 6 was a 1200cpsi cordierite monolith coated with catalyst 2 at a loading of 2g/in³. The monoliths were cored to give cylindrical catalysed components of length 3in (7.5cm) and diameter 1.4in (3.5cm).

5 The pre-heated mix of steam, fuel and air was passed over the catalysed components at a gas hourly space velocity of 139000h⁻¹. The ratio of the gases was O₂:C = 0.375 and H₂O:C = 2.5. The pressure was 2bara. The temperature at the gas inlet was 450°C throughout the 120 hour test. The fuel was a simple gasoline-like fuel containing 0ppm sulphur.

10 Figure 3 shows the NMHC levels for comparative example 2, and examples 5 and 6. The results show that the catalysts according to the invention and the comparative catalyst have comparable durability, with the catalyst performance remaining roughly constant during the test. This durability test was run in the absence of sulphur.

15 Test 4: Carbon Deposition

Two catalysed components were tested. Comparative example 3 was a 900cpsi cordierite monolith coated with comparative catalyst 1 at a loading of 2g/in³. Example 7
20 was a 1200cpsi cordierite monolith coated with catalyst 1 at a loading of 2g/in³. The monoliths were cored to give cylindrical catalysed components of length 3in (7.5cm) and diameter 1.4in (3.5cm).

25 The pre-heated mix of steam, fuel and air was passed over the catalysed components at a gas hourly space velocity of 75000h⁻¹. The ratio of the gases was O₂:C 0.40 and H₂O:C = 0.2. The pressure was 1bara. The temperature at the gas outlet was 650°C throughout the 7 hour test. The fuel was a simple gasoline-like fuel containing 0ppm sulphur.

30 Figure 4 shows the NMHC levels for comparative example 3, and example 7. The catalyst according to the invention has significantly better performance than the comparative catalyst at 650°C. One possible explanation for the improved performance is that the catalyst according to the invention is less susceptible to carbon deposition

(which is usually more extensive at 650°C than at the temperatures employed in tests 1-3).

Test 5: Effect of Ceria-Zirconia loading

5

Eight catalysed components were tested. Comparative example 4 was a 900cpsi cordierite monolith coated with comparative catalyst 2 at a loading of 2g/in³. Examples 8-14 were 900cpsi cordierite monoliths coated with catalysts 3-9 respectively at a loading of 2g/in³. The monoliths were cored to give cylindrical catalysed components of
10 length 3in (7.5cm) and diameter 1.4in (3.5cm).

The pre-heated mix of steam, fuel and air was passed over the catalysed components at a gas hourly space velocity of 115000h⁻¹. The ratio of the gases was O₂:C 0.40 and H₂O:C = 2. The pressure was 1bara. The temperature at the gas inlet was
15 350°C and the temperature at the gas outlet was 690°C. The fuel was a simple gasoline-like fuel containing 0ppm sulphur.

NMHC and CO/CO₂ levels were measured and are shown in the table below:

	Ceria-Zirconia loading (wt%)	Rhodium loading (wt%)	NMHC/dry ppm	CO ₂ /CO
Comparative Example 4	0	1	1320	0.44
Example 8	10	1	3000	0.47
Example 9	30	1	600	1.09
Example 10	40	1	575	1.20
Example 11	60	1	650	1.31
Example 12	30	2	295	1.37
Example 13	40	2	255	1.40
Example 14	60	2	480	1.32

20

The best performance (lowest NMHC and highest CO₂/CO) was observed when the ceria-zirconia loading was 30wt% or 40wt%.

CLAIMS

1. A reforming catalyst comprising precious metal particles dispersed on a support material, wherein the precious metal particles comprise rhodium or ruthenium, wherein
5 the support material comprises ceria and zirconia dispersed on the surface of a silica-alumina material, and wherein the loading of the ceria and zirconia is 10-60wt% based on the weight of the support material.
2. A reforming catalyst according to claim 1, wherein the loading of the ceria and
10 zirconia is 25-60wt% based on the weight of the support material.
3. A reforming catalyst according to claim 1 or claim 2, wherein the surface area of the silica-alumina material is above 100m²/g.
- 15 4. A reforming catalyst according to any preceding claim, wherein the weight ratio of silica to alumina is between 5:100 and 1:1.
5. A reforming catalyst according to any preceding claim, wherein the precious metal particles are rhodium particles or platinum-rhodium alloy particles.
20
6. A reforming catalyst according to claim 5, wherein the precious metal particles are rhodium particles.
7. A reforming catalyst according to any preceding claim, wherein the loading of
25 the precious metal particles is 0.5-10wt%, based on the weight of the support material.
8. A reforming catalyst according to any preceding claim, comprising an alkali metal or alkaline earth metal promoter.
- 30 9. A reforming catalyst according to claim 8, wherein the promoter is lithium.
10. A catalysed component comprising a reforming catalyst according to any one of claims 1 to 9 deposited on a substrate.

11. A catalysed component according to claim 10, wherein the substrate is a monolith, foam, static mixer or heat exchanger unit.

5 12. A catalysed component according to claim 10 or 11, wherein the substrate is ceramic.

13. A catalysed component according to claim 10 or 11, wherein the substrate is metallic.

10

14. A catalysed component according to any one of claims 10 to 13, wherein the amount of catalyst on the support is from 0.5-5g/in³ (0.03-0.3g/cm³).

15 15. A process for reforming fuel using a catalysed component according to any one of claims 10 to 14, wherein the process comprises the step of supplying fuel, steam and optionally air to the catalysed component.

16. A fuel processing system comprising a catalysed component according to any one of claims 10 to 14.

Figure 1

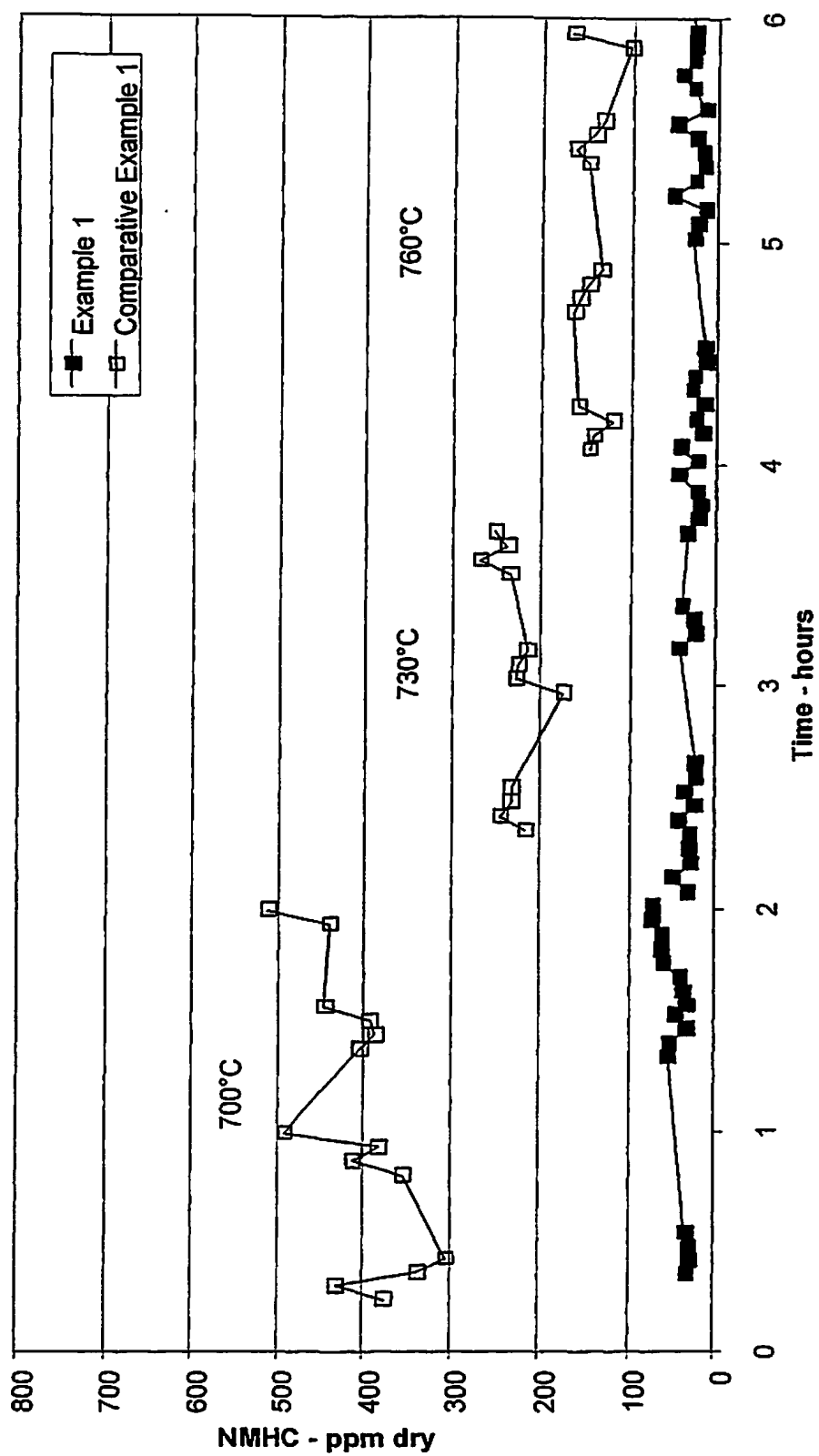


Figure 2

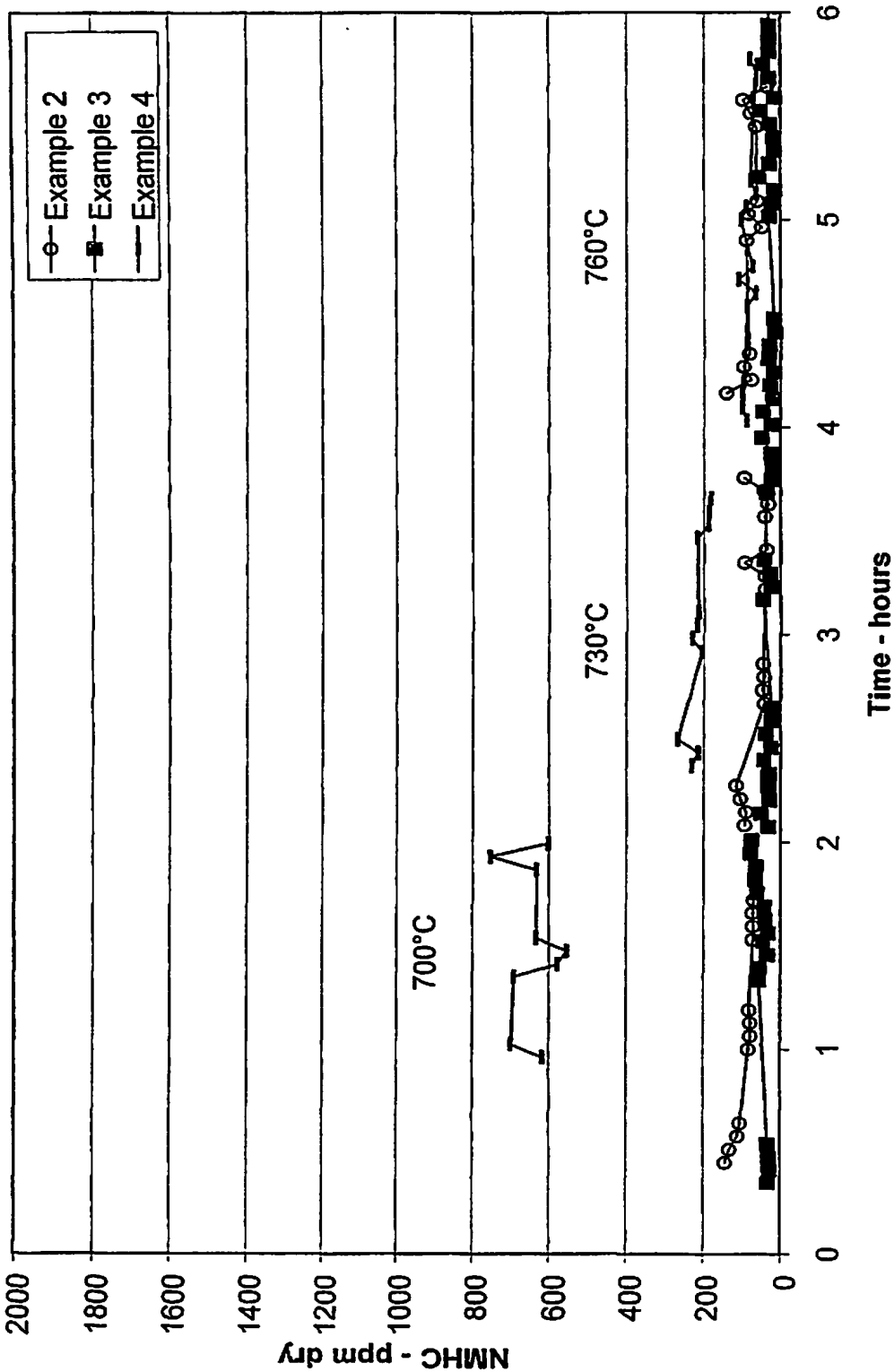


Figure 3

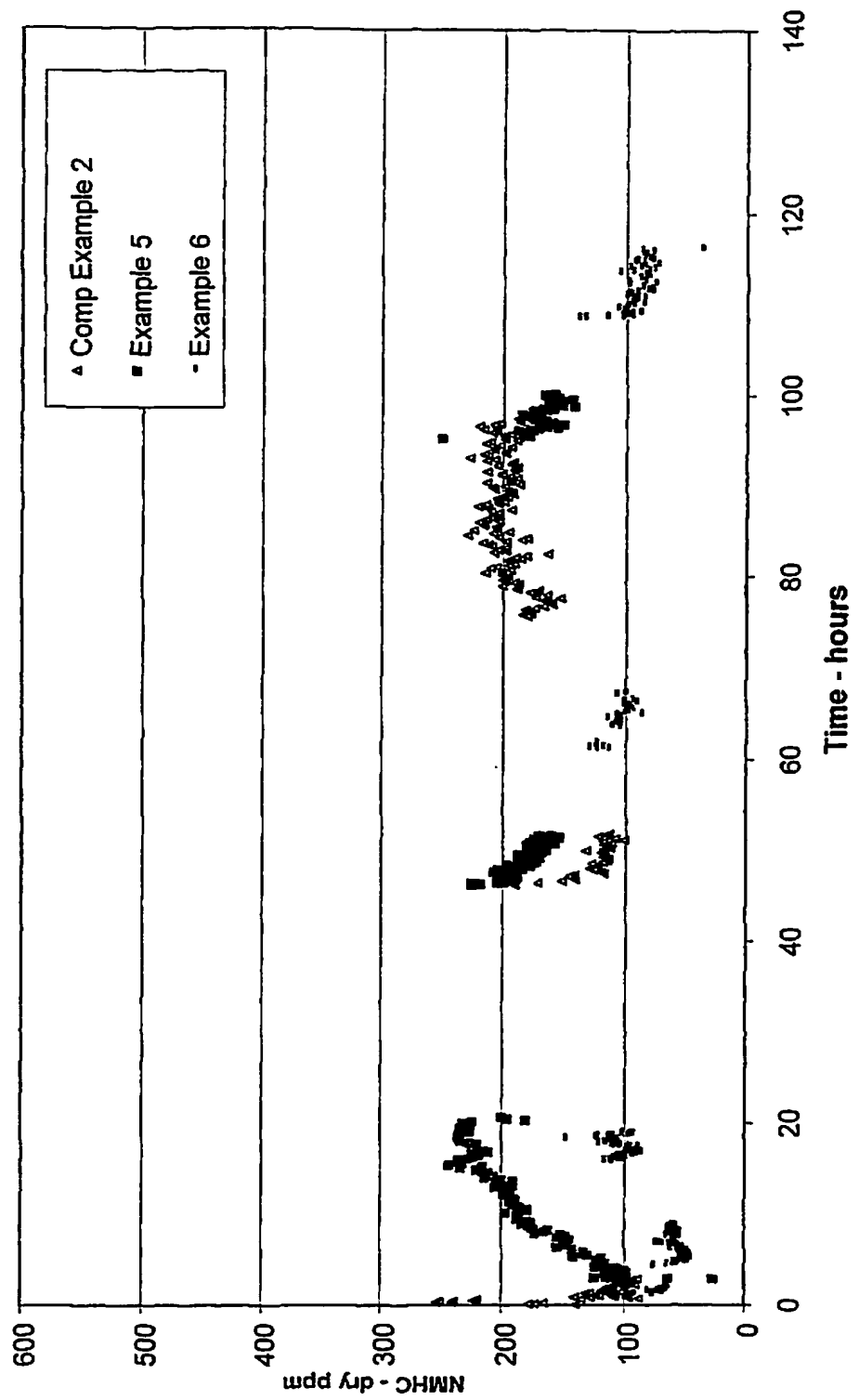
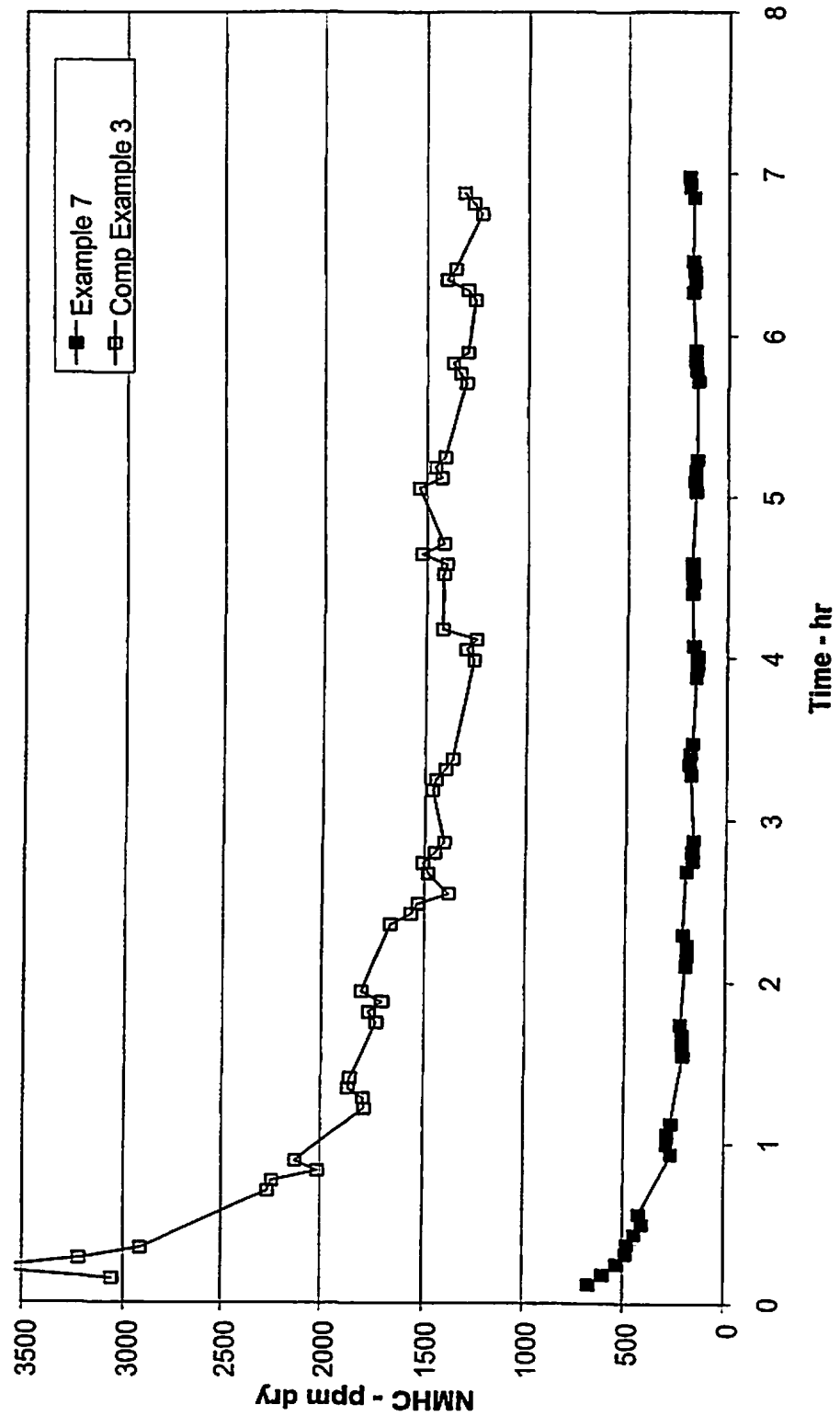


Figure 4



INTERNATIONAL SEARCH REPORT

International application No

PCT/GB 03/05075

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J23/63 B01J21/12 C01B3/40

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, COMPENDEX, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 032 (C-1154), 18 January 1994 (1994-01-18) -& JP 05 261286 A (NISSAN GAADORAA SHOKUBAI KK), 12 October 1993 (1993-10-12) abstract	1-16
Y	PATENT ABSTRACTS OF JAPAN vol. 2003, no. 03, 5 May 2003 (2003-05-05) & JP 2002 336702 A (NIPPON OIL CORP), 26 November 2002 (2002-11-26) cited in the application abstract	1-16
Y	WO 99 48805 A (CARPENTER IAN WILLIAM ; JOHNSON MATTHEY PLC (GB); HAYES JOHN WILLIA) 30 September 1999 (1999-09-30) the whole document	1-16



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

23 February 2004

Date of mailing of the international search report

01/03/2004

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 03/05075

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN vol. 2003, no. 03, 5 May 2003 (2003-05-05) & JP 2002 336701 A (NIPPON OIL CORP), 26 November 2002 (2002-11-26) abstract</p> <p style="text-align: center;">-----</p>	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

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